

Tailor-made polymer electrolytes based upon ionic liquids and their application in all-plastic electrochromic devices

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Abstract

A new type of tailor-made polymer electrolyte based on ionic liquids (ILs) and polymeric ionic liquids (PILs) analogues has been prepared by mixing 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) [bmim][Tf₂N], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] and 1-butyl-3-methylimidazolium bromide [bmim][Br], with poly[1-vinyl-ethyl-imidazolium] bearing similar counter-anions [Tf₂N], [BF₄] and [Br]. The chemical affinity between PILs and ILs affords a completely compatible combination resulting in stable polymer electrolytes. The ionic conductivity of all these polymer electrolytes varies between 10⁻² and 10⁻⁵ S cm⁻¹ at room temperature, and shows high values of conductivity with increasing ionic liquid content. Finally, we have demonstrated that cycle life of electrochromic devices (ECDs) is significantly enhanced (up to 70,000 cycles) when this new type of tailor-made polymer electrolyte was used in PEDOT/electrolyte/PEDOT devices as compared to previously used poly(ethylene oxide) electrolytes.

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1. Introduction

Ionic liquids (ILs) are organic salts with a low melting point (<100 °C) which are being the focus of many investigations because of their chemical stability, low flammability, negligible vapour pressure, high ionic conductivity and wide electrochemical window [1]. In the last decade, ionic liquids have emerged as one of the most promising candidates as liquid electrolytes in advanced electrochemical devices. Pioneering work from D. R. McFarlane and cols. [2] demonstrated that ILs can radically improve the performance, speed, cyclability and long-term stability of electrochromic devices (ECDs) and artificial muscles. The durability of the devices with ILs electrolytes was significantly better than that of traditional organic and aqueous electrolytes. Recent works by various groups has extended

the excellent performance of ILs to other electrochemical devices such as solar cells [3], lithium batteries [4], fuel cells [5] and supercapacitors [6].

Liquid electrolytes do present some drawbacks difficult to overcome, such as leakage. On the other hand, an all-solid state polymer electrolyte has important advantages including mechanical stability, safety and simple processing; but their conductivity is still insufficient for practical use. Two main strategies have been pursued by the scientific community in an attempt to translate the benefits of ILs to polymer electrolytes. The first strategy involves the design of polymer electrolytes composed of conventional polymer matrices and ionic liquids. The second strategy consists of designing functional polymers presenting some of the characteristics of ionic liquids.

Following the first strategy, Carlin and cols. [7,8] reported the synthesis of gel electrolytes prepared from ILs and poly(vinylidene fluoride)-hexafluoropropylene copolymer [PVdF(HFP)]. High-temperature proton conducting membranes based on perfluorinated mem-

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brane-ionic liquid composites have also been described [9,10]. Watanabe and cols. have reported the free radical cross-linking of certain vinyl monomers in ILs, resulting in mechanically strong and highly conductive polymer electrolyte films [11–13]. Passerini and cols. [14,15] have reported flexible solid polymer electrolytes based upon ternary mixtures of ionic liquids with classical PEO/lithium salt binary blends, and their use in lithium metal-polymer electrolyte batteries. Some attempts to introduce ionic liquid into polymer structures to design polymer electrolytes for solid state actuators have been recently published [16,17]. Following the second strategy, pioneering works by Ohno and cols. [18–23] reported the preparation of different types of polymeric ionic liquids (PILs), as a way of developing high performance polymer electrolytes. In our group, we have recently reported a simplified synthetic route to PILs [24,25].

In this work, these two strategies have been combined as a way to develop a novel family of tailor-made polymer electrolytes. Originally, we propose the preparation of ionic liquids (ILs) and polymeric ionic liquids (PILs) mixtures as a route to polymer electrolytes. The use of PILs as the polymer matrix has the main advantage of facilitating the incorporation of the ionic liquid into the PIL matrix. The chemical affinity between polymer and liquid affords a completely compatible and tuneable combination where segregation into two phases has not been observed. To complete this study, we reported the improved performance of all-plastic electrochromic devices using these novel types of tailor-made polymer electrolytes.

2. Experimental

2.1. Synthesis of the ILs and PILs

1-Butyl-3-methyl imidazolium bromide [bmim][Br], 1-ethyl-3-methyl imidazolium bromide [emim][Br], and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonimide) [emim][Tf₂N] were prepared following the procedures described in the literature [26]. Experimental methodology for the synthesis of 1-butyl-3-methylimidazolium bromide [bmim][Br], under vigorous stirring, 20 g (0.146 mol) of bromobutane (99%, Aldrich) was added dropwise to a solution of 11.15 g (0.140 mol) of 1-methylimidazole (99%, Aldrich) in 100 ml of trichloroethylene (Panreac). The mixture was refluxed for 3 h. The resulting yellowish viscous liquid was washed twice with trichloroethylene, decanted and dried under vacuum until constant weight (19.59 g of [bmim][Br] yield: 64%). ¹H NMR (chloroform d, δ/ppm relative to TMS): 10.47 (s, 1H), 7.45 (s, 1H), 7.36 (s, 1H), 4.34 (t, 2H), 4.13 (s, 3H), 1.91 (m, 2H), 1.40 (m, 2H), 0.97 (t, 3H). Purity based on NMR and HPLC >95%.

The other ILs; 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄], 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) [bmim][Tf₂N] and 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆],

were purchased from Solvionic and used as received. The corresponding PILs; poly(1-vinyl-3-methylimidazolium bromide) poly[ViEtIm][Br], poly(1-vinyl-3-methylimidazolium tetrafluoroborate) poly[ViEtIm][BF₄] and poly(1-vinyl-3-methylimidazolium bis(trifluoromethanesulfonimide) poly[ViEtIm][Tf₂N], were synthesized according to the procedure reported before [24,25].

2.2. Preparation of the polymer electrolytes

Polymer electrolytes consisting of different ratios of IL/PIL were prepared by dissolving each PIL in its corresponding IL; poly[ViEtIm][Br] in [bmim][Br], poly[ViEtIm][BF₄] in [bmim][BF₄] and poly[ViEtIm][Tf₂N] in [bmim][Tf₂N]. Tetrahydrofuran was used as a co-solvent when the amount of IL in the mixture was not enough to dissolve the polymer. After mixing the compounds, the polymer electrolytes were dried during 16 h under vacuum.

2.3. Characterization of the polymer electrolytes

¹H NMR spectra were recorded with a Bruker AM 300 (300 MHz) spectrometer. Conductivity measurements of the polymer electrolytes were carried out by the impedance spectroscopy technique, using a potentiostat/galvanostat Autolab PGSTAT30 (Eco Chemie) equipped with a FRA2, at frequencies between 1 MHz and 1 Hz, and the potential amplitude did not exceed 10 mV. The polymer electrolytes were set in a Teflon cell with two platinum electrodes in a constant volume cubical cell (0.5 cm width, 1.0 cm length and 0.0150 cm thick). The cell was placed in a thermostated chamber and the temperature dependence of ionic conductivity was measured while cooling from 75 to 10 °C, under N₂ atmosphere. The same cell and conditions were used for the conductivity measurements of the ILs.

2.4. Construction and characterization of the all-plastic electrochromic devices

In this work we use poly(ethylene dioxythiophene) (PEDOT) covered poly(ethylene terephthalate) foils commercialized by AGFA under the trademark of Orgacon. A thin layer of polymer electrolyte was deposited by casting onto an Orgacon EL-350 foil. As we reported before [27], the device was constructed by sandwiching a second Orgacon EL-350 foil on top of the electrolyte layer. The size of the electrochromic window was 1.5 cm². A standard electrochromic device (ECD) with poly(ethylene glycol) PEO/lithium salt as electrolyte was also constructed to compare the performance of the new tailor-made polymer electrolytes with a traditional polymer electrolyte.

The electrochromic devices were switched using an Autolab PGSTAT30 (Eco Chemie (potentiostat/galvanostat)). Optical characterization of the devices was carried out using a Shimadzu 1603 UV–vis spectrophotometer. The optical contrast (ΔOD) of the ECD was measured at

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